

10/519142

**PCT**  
**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**  
(PCT Article 36 and Rule 70)

REC'D 13 OCT 2004

WIPO PCT

Applicant's or agent's file reference 31759PC01	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/DK 03/00439	International filing date (day/month/year) 25.06.2003	Priority date (day/month/year) 25.06.2002
International Patent Classification (IPC) or both national classification and IPC C01G23/04		
Applicant AALBORG UNIVERSITET et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

- I  Basis of the opinion
- II  Priority
- III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV  Lack of unity of invention
- V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI  Certain documents cited
- VII  Certain defects in the international application
- VIII  Certain observations on the international application

Date of submission of the demand 19.01.2004	Date of completion of this report 11.10.2004
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Mayne, J Telephone No. +49 89 2399-8572



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/DK 03/00439

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, Pages**

1-23 as originally filed

**Claims, Numbers**

1-74 filed with telefax on 27.09.2004

**Drawings, Sheets**

1/5-5/5 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/DK 03/00439

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).  
*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	1-63, 65, 72-74
	No: Claims	64, 66-71
Inventive step (IS)	Yes: Claims	1-63, 72-74
	No: Claims	64-71
Industrial applicability (IA)	Yes: Claims	1-74
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/DK 03/00439

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

I Reference is made to the following documents:

- D1: US-B1-6 387 341
- D2: TADAO SUGIMOTO ET AL: 'Synthesis of uniform anatase TiO<sub>2</sub> nanoparticles by gel-sol method: 3. Formation process and size control' JOURNAL OF COLLOID AND INTERFACE SCIENCE, vol. 259, no. 1, 1 March 2003, pages 43-52
- D3: EP-A-0366825
- D4: GB-A-633,845

The documents D3 and D4 were not cited in the international search report. Copies of the documents were appended to the written opinion.

**Article 33(2) PCT**

II Claims 1-63

D1 is the closest prior art for the method of claim 1. It discloses a method of manufacturing metal oxides from organo-metallic precursors, such as alkoxides, by bringing the precursor(s) into contact with a reaction medium comprising supercritical CO<sub>2</sub>. A cosolvent can also be present (col. 3, l. 6-col. 4, l. 7).

D1 does not mention the presence of a solid reactor filling material.

Claim 1 is therefore novel.

Claims 1-63 fulfill the requirements of Article 33(2) PCT.

III Independent claims 64-71

Independent claims 64-71 are each directed to a product which has been made by a method according to claims 1-63.

A product must fulfill the requirements of novelty and inventive step regardless of its method of manufacture. A product is not automatically novel even if produced by a

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/DK 03/00439

novel process.

1. D1 (example 2) discloses the production of TiO<sub>2</sub> from the metal alkoxide using a supercritical solvent, CO<sub>2</sub>. SEM observations of the sample C2 RES (Table 6) reveal non-agglomerated spherical particles with sizes in the range 0.1 μm to 1 μm. The particle size does not increase on calcination at 480°C which results in the crystalline form anatase (col. 14, l. 32-44).  
This anticipates the subject matter of claims 66-68.
2. The product of sample C2 SC1 (D1, Table 6) is in the form of spherical grains in a cluster with grain diameter 0.2 to 1.5 μm, i.e. primary particles have been aggregated to form clusters. At least some of these spherical grains have a size less than 1000 nm (1 μm) since 200 nm is the lower limit of the size range.  
This anticipates the subject matter of claim 64.
3. Submicron sized particles of TiO<sub>2</sub> anatase are also known from D2 (p. 44, right column, 2nd paragraph, §2.2 1st line, §3.1 1st paragraph, §3.2 1st paragraph, Fig. 5).  
This anticipates the subject matter of claims 66-68.
4. Submicron sized boehmite is known, see D3, p. 3, l. 30-38 and claims 13 and 14.  
This anticipates the subject matter of claims 69 and 70.
5. Submicron sized aluminium hydroxide is known, see D4, p. 2, l. 102-125.  
This anticipates the subject matter of claim 71.

Claims 64, 66-71 do not fulfill the requirements of Article 33(2) PCT.

6. The subject matter of claim 65 is not seen in D1.  
Claim 65 fulfills the requirements of Article 33(2) PCT.

**IV Claims 72-74**

D1 (Fig. 1, col. 7, l. 40-col. 8, l. 2) discloses an apparatus for manufacturing a metal oxide which comprises a reactor (11), means for introducing a co-solvent from reservoir (13) via circuit (4) and means for introducing a supercritical solvent from reservoir (3) via circuit (4).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/DK 03/00439

The reactor (11) is a pressurizable sealed vessel such as an autoclave and contains the alkoxide precursor charge. Hence there must be means to introduce the metal-containing precursor into the reactor. In the case of an autoclave this can be done by removing the lid in the unpressurized state.

D1 does not disclose an apparatus with a reactor containing a solid reactor filling material.

Claims 72-74 fulfill the requirements of Article 33(2) PCT.

Article 33(3) PCT

V    Claims 1-63, 72-74

As mentioned above (§II) D1 does not mention using a solid reactor filling material in the reaction to form the metal oxide.

According to the description (p. 6, l. 30 - col. 7, l. 5) the solid reactor filling material solves the problem of removal of the nanoparticulate product from the reactor without the need for costly treatments such as plasma treatment or calcination. This was not foreseeable from D1.

Claims 1-63 and 72-74 fulfill the requirements of Article 33(3) PCT.

VI    Claim 65

The method of D1, example 2, is capable of producing spherical grains of TiO<sub>2</sub> with grain diameter about 0.1 μm, sample E4 SLC. Nothing critical or unexpected has been demonstrated for these particles to be aggregated as in claim 65.

Claim 65 does not fulfill the requirements of Article 33(3) PCT.

Article 5 PCT

Claim 3 says that the product is "substantially crystalline". This implies a figure equal to or close to 100%. However, the highest level of crystallinity that has been produced

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/DK 03/00439

is  $40.0 \pm 5.0\%$ , see Tables 5 and 8. There is no teaching in the application as to how to produce a metal oxide, metal oxyhydroxide or metal hydroxide which is substantially crystalline using the method steps of claim 1.

Hence it is not known from the application how to carry out the method of claim 3.

Article 6 PCT

1. The subject matter of claim 1 is a method. However, the features of claims 3-5 concern the nature of the product resulting from the method, with no indication of what additional method step is required to yield the stated product. Hence the same method steps lead to a substantially crystalline product, an amorphous product or a mixture of several different phases.
2. Claims 60-63 depend on claim 57 but contradict it. According to claim 57 there are no further treatments of the solid reactor filling material. However, claims 60-63 provide for the further treatments of flushing in a fluid, vacuum means; blowing means and ultrasonic means respectively.